

TITLE OF THE INVENTION

METHOD OF MANUFACTURING SYNTHESIS GAS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application is based upon and claims the benefit of priority from the prior Japanese Patent Application No. 2000-246913, filed August 16, 2000, the entire contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

10 This invention relates to a method of manufacturing a synthesis gas to be employed for the synthesis of gasoline, methanol or dimethyl ether by way of the GTL (Gas to Liquid) process.

15 A synthesis gas comprising hydrogen (H_2) and carbon monoxide (CO) has been employed as a raw material for the synthesis of gasoline, etc. by way of the GTL (Gas to Liquid) process according to the Fisher-Tropsch reaction system.

20 This synthesis gas has been conventionally manufactured by a method wherein steam and carbon dioxide are added at first to a natural gas employed as a raw gas to prepare a mixed gas, which is then fed to the reaction tube of reformer which has been heated to a predetermined temperature so as to steam-reform the
25 natural gas together with carbon dioxide, thereby manufacturing the synthesis gas containing hydrogen (H_2) and carbon monoxide (CO).

By the way, depending on the place of origin, the natural gas occasionally contains hydrogen sulfide (H_2S) and carbon dioxide (for example, CO_2 : 7.1% by volume, and H_2S : 0.6% by volume). When such a natural gas is to be employed as a raw material, it is usually practiced to remove hydrogen sulfide prior to the step of adding steam and carbon dioxide to the natural gas. In this case, the removal of hydrogen sulfide from the natural gas is conventionally performed by means of amine absorption method.

However, if it is desired to remove hydrogen sulfide to a level of the order of ppm by means of the amine absorption method, carbon dioxide included in the original natural gas is also removed together with hydrogen sulfide. As a result, it becomes impossible to utilize the carbon dioxide that has been originally included in the natural gas, so that a large quantity of carbon dioxide is required to be supplied to the natural gas prior to the stage where the natural gas is to be transferred to the reaction tube of the reformer, thus increasing the manufacturing cost of the synthesis gas.

BRIEF SUMMARY OF THE INVENTION

Therefore, an object of this invention is to provide a method for manufacturing a synthesis gas, which makes it possible to effectively utilize the carbon dioxide in a natural gas containing hydrogen

sulfide and carbon dioxide by selectively removing only the hydrogen sulfide therefrom in the synthesis gas manufacturing method employing a reformer, thereby making it possible to reduce the quantity of carbon dioxide to be added to the natural gas prior to the stage where the natural gas is to be transferred to the reformer.

Namely, this invention provides a method of manufacturing a synthesis gas containing hydrogen and carbon monoxide, which comprises steps of;

removing only hydrogen sulfide from a natural gas containing hydrogen sulfide and carbon dioxide by permitting the natural gas to pass through a hydrogen sulfide-removing device filled with a hydrogen sulfide absorbent;

adding carbon dioxide and steam to the natural gas which the hydrogen sulfide has been removed to prepare a mixed gas; and

feeding the mixed gas into a reaction tube of a reformer, thereby permitting mainly a steam reforming reaction to take place in the mixed gas.

The method of manufacturing a synthesis gas according to this invention may be performed in such a way that before the natural gas is fed to the hydrogen sulfide-removing device, the natural gas is forced to pass through a convection portion communicated with a combustion radiation portion of the reformer, thereby

heating the natural gas up to a temperature which is suited for the reaction between the hydrogen sulfide in the natural gas and the hydrogen sulfide adsorbent.

The method of manufacturing a synthesis gas according to this invention may be performed in such a way that the carbon dioxide recovered from a combustion exhaust gas generated at the combustion radiation portion of the reformer is utilized as a carbon dioxide source.

The method of manufacturing a synthesis gas according to this invention may be performed in such a way that the carbon dioxide recovered from the synthesis gas at a downstream side of the reformer is utilized as a carbon dioxide source.

It is preferable in the method of manufacturing a synthesis gas according to this invention that the hydrogen sulfide adsorbent is at least one oxide selected from triiron tetraoxide (Fe_3O_4) and zinc oxide (ZnO).

It is preferable in the method of manufacturing a synthesis gas according to this invention that the hydrogen sulfide-removing device is provided with at least one unit of first desulfurizing column filled with the hydrogen sulfide adsorbent comprising triiron tetraoxide and with a second desulfurizing column filled with the hydrogen sulfide adsorbent comprising zinc oxide, and that the natural gas containing

hydrogen sulfide and carbon dioxide is permitted to successively pass through one column selected from these first desulfurizing columns and second desulfurizing column.

5 It is preferable that the hydrogen sulfide-removing device is provided with at least three units of first desulfurizing columns to be filled with triiron tetraoxide, wherein a first placed first desulfurizing column among the first
10 desulfurizing columns is designed to execute an adsorption operation of hydrogen sulfide, a second placed first desulfurizing column among the first desulfurizing columns is designed to execute an operation of regenerating the adsorbent (iron sulfide)
15 on which hydrogen sulfide is adsorbed, and a third placed first desulfurizing column among the first desulfurizing columns is designed to execute an operation of reducing the adsorbent that has been regenerated, these operations being sequentially
20 executed.

 Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects
25 and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate presently preferred embodiments of the invention, and together with the general description given above and the detailed description of the preferred embodiments given below, serve to explain the principles of the invention.

FIG. 1 is a flow chart illustrating main manufacturing steps of synthesis gas in a synthesizing plant of gasoline, kerosene and gas oil, which is employed in an embodiment of this invention; and

FIG. 2 is a flow chart illustrating the hydrogen sulfide-removing device which is adapted to be incorporated in the synthesizing plant of FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

Next, the method of manufacturing a synthesis gas (which is suited for use in synthesizing for example gasoline, kerosene and gas oil) will be explained with reference to the accompanying drawings.

FIG. 1 is a flow chart illustrating main manufacturing steps of synthesis gas in a synthesizing plant of gasoline, kerosene and gas oil, which is employed in an embodiment of this invention.

Referring to FIG. 1, a reformer 10 comprises a reaction tube 11 adapted to be employed for steam reforming, a combustion radiation portion 12 disposed

around the reaction tube 11 and designed to heat the reaction tube through the combustion of fuel, and a chimney 14 which is communicated via a convection portion (waste heat recovering portion) 13 with the combustion radiation portion 12. The reaction tube 11 is filled therein with a nickel-based catalyst for instance. A fuel-introducing passageway 20₁ is communicated with the combustion radiation portion 12 of the reformer 10.

A natural gas-introducing passageway 20₂ is communicated via a convection portion 13 of the reformer 10 with a hydrogen sulfide-removing device 30. As shown in FIG. 2, this hydrogen sulfide-removing device 30 is provided with three units of first desulfurizing columns 31₁ to 31₃, each filled with a hydrogen sulfide adsorbent such as triiron tetraoxide (Fe₃O₄) particles. Three natural gas-introducing branch passageways 32₁ to 32₃ which are branched from the natural gas-introducing passageway 20₂ are communicated with the top portions of the first desulfurizing columns 31₁ to 31₃, respectively. Natural gas inlet on-off valves 33₁ to 33₃ are attached to the natural gas-introducing branch passageways 32₁ to 32₃, respectively. The bottom portions of the first desulfurizing columns 31₁ to 31₃ are connected, via natural gas-discharging branch passageways 34₁ to 34₃ and via a passageway 35 with which these natural

gas-discharging branch passageways 34₁ to 34₃ are combined, with a top portion of a second desulfurizing column 36 filled with zinc oxide particles employed as a hydrogen sulfide absorbent. The bottom portion of the second desulfurizing column 36 is connected with a raw gas-introducing passageway 20₃ to be explained hereinafter. Natural gas outlet on-off valves 37₁ to 37₃ are attached to the natural gas-discharging branch passageways 34₁ to 34₃, respectively.

A sulfur recovery device 38 is communicated through a passageway 39₁ with a circulating gas blower 40. This circulating gas blower 40 is communicated through a passageway 39₂ with a preheater 41. Air is supplied to the hydrogen sulfide-removing device 30 via a passageway 39₃ disposed in the vicinity of the circulating gas blower 40. The passageway 39₂ is provided with a gas-gas heat exchanger 42 for executing a heat exchange between the gas mixed with the air from the circulating gas blower 40 and the heated sulfur dioxide gas that has been discharged from the first desulfurizing column provided for executing the regeneration process (to be explained hereinafter). The preheater 41 is communicated via a passageway 39₄ and three branch passageways 43₁ to 43₃ branched from the passageway 39₄ with each of the bottom portions of the first desulfurizing columns 31₁ to 31₃. Air-containing gas inlet on-off valves 44₁ to 44₃ are

attached to the branch passageways 43₁ to 43₃,
respectively. The top portions of the first
desulfurizing columns 31₁ to 31₃ are connected, via
sulfur dioxide gas-discharging branch passageways 45₁
5 to 45₃ and via a passageway 39₅ with which these
branch passageways 45₁ to 45₃ are combined, with
the sulfur recovery device 38. Sulfur dioxide gas
outlet on-off valves 46₁ to 46₃ are attached to
the branch passageways 45₁ to 45₃, respectively.
10 The passageway 39₅ is provided with the aforementioned
gas-gas heat exchanger 42.

A reducing gas-introducing passageway 47 is
branched at the distal end thereof, thus forming three
branch passageways 48₁ to 48₃ which are communicated
15 with top portions of the first desulfurizing columns
31₁ to 31₃, respectively. Reducing gas on-off valves
49₁ to 49₃ are attached to the branch passageways 48₁
to 48₃, respectively.

The hydrogen sulfide-removing device 30
20 constructed as explained above is communicated, via
a raw gas-introducing passageway 20₃ which is disposed
so as to pass through the convection portion 13, with
a top portion of the reaction tube 11. A distal end of
steam-introducing passageway 20₄ is communicated with
25 the raw gas-introducing passageway 20₃ through a midway
portion thereof which is located on the downstream side
of the hydrogen sulfide-removing device 30 and also on

the upstream side of the convection portion 13.

A first carbon dioxide recovery device 51₁ is disposed at the convection portion 13 of the reformer 10, thereby enabling carbon dioxide to be recovered from the combustion exhaust gas of the convection portion 13. This carbon dioxide recovery device 51₁ is connected via the passageway 20₅ with a compressor 52. This compressor 52 is communicated, via a passageway 20₆, with a midway portion of the raw gas-introducing passageway 20₃ which is located on the downstream side of the hydrogen sulfide-removing device 30 and also on the upstream side of the convection portion 13.

One end of synthesis gas passageway 20₇ is connected with a lower end portion of the reaction tube 11 of the reformer 10 and the other end thereof is connected with the Fisher-Tropsch (FT) reaction system 53 which is filled with a cobalt-based catalyst for instance. By the way, the catalyst to be filled in this FT reaction system 53 may not be confined to the cobalt-based catalyst but may be an iron-based catalyst for instance. A heat exchanger 54 and a second carbon dioxide recovery device 51₂ are disposed on the downstream side of the reformer 10 and successively arranged in the mentioned order on the synthesis gas passageway 20₇. This heat exchanger 54 is disposed enabling a passageway 20₈ to intersect

therewith so as to heat for example a boiler water passing through this passageway 20₈, thereby generating a high-pressure steam. The second carbon dioxide recovery device 51₂ is connected via a passageway 20₉ with the compressor 52. By the way, a passageway 20₁₀ for passing a boiler water for instance is disposed to intersect with the convection portion 13 of the reformer 10, thereby enabling a heat exchange to be executed between the combustion exhaust gas of the convection portion 13 and the boiler water. As a result, the combustion exhaust gas is cooled and at the same time, the boiler water itself is heated to generate a high-pressure steam.

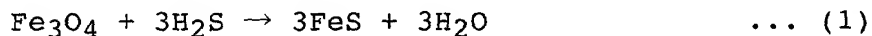
Next, the method of manufacturing a synthesis gas will be explained with reference to the synthesizing plant shown in FIGS. 1 and 2.

First of all, a fuel for combustion is fed via the fuel-introducing passageway 20₁ to the combustion radiation portion 12 of the reformer 10 so as to allow the fuel to burn together with air, thereby heating the interior of reaction tube 11 up to a sufficiently high temperature (for example, 850-900°C). This heating of the reaction tube 11 is performed because this reforming reaction at the reformer 10 is an endothermic reaction. The combustion exhaust gas containing carbon dioxide and generated at this combustion radiation portion 12 is allowed to flow via the convection

portion 13 into the chimney 14. As the combustion exhaust gas passes through the convection portion 13, the combustion exhaust gas is heat-exchanged with the natural gas passing through the natural gas-introducing passageway 20₂, with the after-mentioned natural gas mixed with carbon dioxide and steam and passing through the raw gas-introducing passageway 20₃, and also with the boiler water passing through the passageway 20₁₀, thereby cooling the combustion exhaust gas. The carbon dioxide in the combustion exhaust gas thus cooled is recovered by the first carbon dioxide recovery device 51₁ and then, fed via the passageway 20₅ to the compressor 52. The combustion exhaust gas thus cooled and depleted of carbon dioxide is released via the chimney 14 to air atmosphere.

Natural gas containing methane as a main component and also containing hydrogen sulfide and carbon dioxide is fed to the natural gas-introducing passageway 20₂ and allowed to pass through this passageway 20₂ and hence through the convection portion 13 of the reformer 10, during which the natural gas is heated up to a temperature (for example, 400°C) which is optimal for the reaction between the hydrogen sulfide and the triiron tetraoxide (Fe₃O₄) employed as a hydrogen sulfide adsorbent (to be explained hereinafter). The natural gas thus heated is introduced into the hydrogen sulfide-removing device 30. The natural

gas inlet on-off valve 33₁ attached to the natural
gas-introducing branch passageway 32₁ attached to the
natural gas-discharging branch passageway 34₁ are
respectively opened in this hydrogen sulfide-removing
5 device 30, the aforementioned heated natural gas is
allowed to enter only into the first desulfurizing
column 31₁ (positioned on the left side of FIG. 2)
which is filled with the triiron tetraoxide (Fe₃O₄)
particles. Then, in this first desulfurizing column
10 31₁, the hydrogen sulfide (H₂S) in the natural gas is
permitted to react with the triiron tetraoxide (Fe₃O₄)
particles at the aforementioned temperature (400°C)
according to the following reaction formula (1),
thereby enabling most of the hydrogen sulfide to be
15 removed from the natural gas.



The natural gas that has passed through the first
desulfurizing column 31₁ is then fed, via the natural
gas-discharging branch passageway 34₁ and the
20 passageway 35, to the second desulfurizing column 36
which is filled with the zinc oxide (ZnO) particles.
Then, in this second desulfurizing column 36, any
residual hydrogen sulfide left in the natural gas is
permitted to react with the zinc oxide (ZnO) particles
25 according to the following reaction formula (2),
thereby enabling the residual hydrogen sulfide to be
removed from the natural gas.



In the process wherein the natural gas containing hydrogen sulfide and carbon dioxide is permitted to pass through the first desulfurizing column 31₁ which is filled with the triiron tetraoxide (Fe₃O₄) particles and then through the second desulfurizing column 36 which is filled with the zinc oxide (ZnO) particles, only the hydrogen sulfide is enabled to be removed to a level in the order of ppm without allowing the carbon dioxide to be removed from the natural gas in contrast with the conventional amine absorption method.

When the desulfurizing performance of the triiron tetraoxide (Fe₃O₄) particles filled in the first desulfurizing column 31₁ which is disposed on the left side in FIG. 2 among these three units of the first desulfurizing columns 31₁ to 31₃ is deteriorated due to the reaction thereof to remove hydrogen sulfide from the natural gas, the feeding of the natural gas may be successively switched from this first desulfurizing column 31₁ to the first desulfurizing column 31₂ which is disposed at the center in FIG. 2, and subsequently, to the first desulfurizing column 31₃ which is disposed on the right side in FIG. 2, thereby enabling the hydrogen sulfide to be continuously removed from the natural gas.

Once the desulfurizing performance of one of the first desulfurizing columns is deteriorated due

to the desulfurizing operation thereof, that first desulfurizing column (for example, the first desulfurizing column 31₂ which is disposed at the center in FIG. 2) is subjected to the regeneration treatment as follows. Namely, the air-containing gas inlet on-off valve 44₂ attached to the branch passageway 43₂ as well as the sulfur dioxide gas outlet on-off valve 46₂ attached to the sulfur dioxide gas-discharging branch passageway 45₂ are respectively opened at first. Subsequently, the circulating gas blower 40 is actuated to thereby introduce the gas (mainly nitrogen gas) that has been separated by the sulfur recovery device 38 into the gas-gas heat exchanger 42 via the passageways 39₁ and 39₂, and at the same time, air is supplied via the passageway 39₃ to the passageway 39₂. The gas mainly consisted of air that has been heat-exchanged with the heated sulfur dioxide gas (to be explained hereinafter) at the gas-gas heat exchanger 42 is fed through the passageway 39₄ and the branch passageway 43₂ to a lower portion of the first desulfurizing column 31₂. In the course of process wherein the gas mainly consisted of air is permitted to pass through the passageway 39₄, the gas mainly consisted of air is heated up to a temperature (for example, 600°C) which is optimal for the regeneration of iron sulfide (FeS) (to be explained hereinafter) by means of the preheater 41 attached to

the passageway 39₄. When this heated gas mainly consisted of air is introduced into the first desulfurizing column 31₂, the iron sulfide (FeS) produced in the aforementioned desulfurization operation as shown by the aforementioned reaction formula (1) is reacted with oxygen according to the following reaction formula (3), thereby producing diiron trioxide (Fe₂O₃) and sulfur dioxide gas (SO₂), thus accomplishing the regeneration.



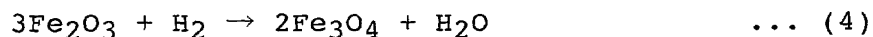
The sulfur dioxide gas that has been generated at the first desulfurizing column 31₂ is then transferred via the sulfur dioxide gas-discharging branch passageway 45₂ and the passageway 39₅ to the sulfur recovery device 38. In the course of process wherein the sulfur dioxide gas passes through the passageway 39₅, it is heat-exchanged with the gas mainly consisted of air at the gas-gas heat exchanger 42 which is attached to the passageway 39₅, thereby cooling the sulfur dioxide gas. This cooled sulfur dioxide gas is then transferred to the sulfur recovery device 38 in which sulfur is recovered from the sulfur dioxide gas.

Meanwhile, at the first desulfurizing columns which is filled with the hydrogen sulfide adsorbent that has undergone the aforementioned regeneration treatment (for example, the first desulfurizing column 31₃ which is disposed on the right side in

FIG. 2), the reduction treatment of the hydrogen sulfide adsorbent will be performed as follows.

Namely, the reducing gas on-off valve 49₃ attached to the branch passageway 48₃ is opened at first.

5 Then, a reducing gas (for example, hydrogen gas) is fed via the reducing gas-introducing passageway 47 and the passageway 48₃ to a top portion of the first desulfurizing column 31₃. When hydrogen gas is introduced into this first desulfurizing column 31₃,
10 the diiron trioxide (Fe₂O₃) that has been produced through the regeneration operation as shown by the aforementioned reaction formula (3) is reacted with the hydrogen gas as shown by the reaction formula (4) to thereby produce triiron tetraoxide (Fe₃O₄) to be
15 employed in the desulfurization and water (H₂O). The water thus produced is transferred from the natural gas-discharging branch passageway 34₃ via a passageway (not shown) to the first desulfurizing column for executing the desulfurizing operation (for example,
20 the first desulfurizing column 31₁ which is disposed on the left side in FIG. 2).



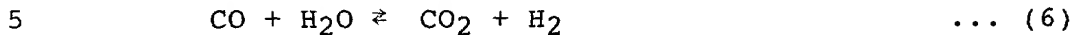
All of these desulfurizing operation, regenerating operation and reducing operation are concurrently
25 performed in order to smoothly perform the desulfurization.

The natural gas thus depleted of hydrogen sulfide

is fed to the raw gas-introducing passageway 20₃.
On this occasion, the carbon dioxide that has been
compressed by the compressor 52 is added via the
passageway 20₆ to the natural gas at a predetermined
5 ratio to prepare a carbon dioxide-containing
natural gas. Further, steam is also added via
the steam-introducing passageway 20₄ to the carbon
dioxide-containing natural gas at a predetermined
ratio to prepare a mixed gas. By the way, as for this
10 steam, the steam that has been generated through a heat
exchange between the boiler water and the synthesis gas
at the heat exchanger 54 as well as the steam that has
been generated through a heat exchange between the
boiler water and the combustion exhaust gas at the
15 convection portion 13 of reformer 10 can be utilized.

The mixed gas, i.e., the natural gas mixed with
carbon dioxide and steam is allowed to flow inside the
raw gas-introducing passageway 20₃ and preheated as
this mixed gas passes through the convection portion 13
20 of reformer 10, after which this mixed gas thus
preheated is fed to the reaction tube 11. The natural
gas containing methane (CH₄) as a main component, steam
and carbon dioxide, which have been fed to the reaction
tube 11 of the reformer 10 are then subjected to steam
25 reforming process wherein methane is mainly steam-
reformed under the presence of a catalyst disposed
inside the reaction tube 11, thereby manufacturing

a synthesis gas containing hydrogen gas, carbon monoxide and carbon dioxide according to the following formulas (5) and (6).



In these formulas (5) and (6) of the reforming reaction, 4 moles of hydrogen and one mole of carbon dioxide can be produced through the reaction between one mole of methane and 2 moles of steam. In the
10 actual reaction system however, a composition which is close to a chemical equilibrium composition that can be determined by the temperature and pressure at the outlet of the reaction tube can be obtained.

Therefore, it would be possible to manufacture a
15 synthesis gas containing hydrogen gas, carbon monoxide and carbon dioxide with a molar ratio of H_2/CO ranging from 1 to 2.5 by setting the contents of methane of the natural gas, steam and carbon dioxide to such that the molar ratio between methane (CH_4) and steam (H_2O)
20 falls within the range of: $\text{CH}_4:\text{H}_2\text{O} = 1:1.5$ to $1:3$; while the molar ratio between methane (CH_4) and carbon dioxide (CO_2) falls within the range of: $\text{CH}_4:\text{CO}_2 = 1:1$ to $1:3$ on the occasion of adding steam and carbon dioxide to the natural gas.

25 The synthesis gas thus obtained is fed via a synthesis gas passageway 207 to the heat exchanger 54 to thereby heat the boiler water flowing through

the passageway 20₈ to generate a high-pressure steam. Concurrently, the synthesis gas itself is cooled and then, fed to the second carbon dioxide recovery device 51₂, in which the carbon dioxide in the
5 natural gas is recovered, and the water concurrently generated is discharged outside the system through a passageway 20₁₁. The carbon dioxide thus recovered is transferred via the passageway 20₉ to the compressor 52 and compressed together with the carbon dioxide that
10 has been recovered at the first carbon dioxide recovery device 51₁, the carbon dioxide thus compressed being subsequently added via the passageway 20₆ to the natural gas existing inside the raw gas-introducing passageway 20₃.

15 The synthesis gas thus depleted of carbon dioxide is then transferred via the passageway 20₇ to the Fisher-Tropsch (FT) reaction system 53 which is filled with a cobalt-based catalyst for instance, thereby allowing the hydrogen and carbon monoxide all included
20 in the synthesis gas to react with each other, thus synthesizing gasoline, kerosene and gas oil.

According to this embodiment, before the step of adding carbon dioxide and steam to a natural gas containing hydrogen sulfide and carbon dioxide, the
25 natural gas is allowed to pass through the hydrogen sulfide-removing device 30 filled with a hydrogen sulfide adsorbent to thereby selectively removing

the hydrogen sulfide from the natural gas without allowing the carbon dioxide to be removed from the natural gas in contrast with the conventional amine absorption method. Therefore, it is possible according to this invention to effectively utilize the carbon dioxide of the natural gas and to reduce the quantity of carbon dioxide to be added to the natural gas prior to the stage of introducing the natural gas into the reformer. As a result, it is possible to reduce the manufacturing cost of the synthesis gas.

In particular, before the natural gas containing hydrogen sulfide and carbon dioxide is fed to the hydrogen sulfide-removing device 30, the natural gas is allowed to pass through the natural gas-introducing passageway 20₂ which is designed to pass through the convection portion 13 of the reformer 10, thereby heating up the natural gas to a temperature which is optimal for the reaction between the hydrogen sulfide in the natural gas and the triiron tetraoxide filled in the first desulfurizing columns 31₁ to 31₃ of the hydrogen sulfide-removing device 30, thus making it possible to reduce the quantity of fuel to be used for the removal of the hydrogen sulfide.

Further, as seen from the hydrogen sulfide-removing device 30 shown in FIG. 2, since the natural gas containing hydrogen sulfide and carbon dioxide is permitted to pass through the first desulfurizing

column 31₁ which is filled with the triiron tetraoxide (Fe₃O₄) particles (the first desulfurizing column 31₁ which is disposed on the left side in FIG. 2) and then through the second desulfurizing column 36 which is filled with the zinc oxide (ZnO) particles, it is now possible to selectively remove only the hydrogen sulfide to a level in the order of ppm from the natural gas.

As a matter of fact, when a natural gas having a composition of: CH₄; 86.5 vol.%, C₂H₆; 1.8 vol.%, N₂; 4.0 vol.%, CO₂; 7.1 vol.% and C₂S; 0.6 vol.% was treated by means of the hydrogen sulfide-removing device 30 shown in FIG. 2 by allowing it to pass through the first desulfurizing column 31₁ which is filled with the triiron tetraoxide (Fe₃O₄) particles (the first desulfurizing column 31₁ which is disposed on the left side in FIG. 2) and then through the second desulfurizing column 36 which is filled with the zinc oxide (ZnO) particles, it was possible to obtain a natural gas having a composition of: CH₄; 87.0 vol.%, C₂H₆; 1.8 vol.%, N₂; 4.1 vol.%, CO₂; 7.1 vol.% and C₂S; 1ppm or less. Namely, it was possible to leave the carbon dioxide remain almost entirely in the raw natural gas and at the same time, to selectively remove most of the hydrogen sulfide.

Furthermore, as seen from the hydrogen sulfide-removing device 30 shown in FIG. 2, since three units

of first desulfurizing columns 31₁ to 31₃ each filled with the triiron tetraoxide (Fe₃O₄) particles are juxtaposed, enabling a first placed first desulfurizing column to execute an adsorption operation of hydrogen sulfide, enabling a second placed first desulfurizing column to execute an operation of regenerating the adsorbent adsorbed with hydrogen sulfide, also enabling a third placed first desulfurizing column to execute an operation of reducing the adsorbent that has been regenerated, and further enabling these operations to be sequentially executed, it becomes possible to more smoothly and effectively remove the hydrogen sulfide from the natural gas.

To the natural gas thus depleted of hydrogen sulfide by way of the aforementioned procedures, steam and carbon dioxide are added to obtain a mixed gas, which is then fed to the reaction tube 11 of the reformer 10 to execute the steam reforming of the mixed gas, thereby manufacturing a synthesis gas with a molar ratio of H₂/CO ranging from 1 to 2.5. This synthesis gas having such a molar ratio of H₂/CO is then fed to the Fisher-Tropsch (FT) reaction system 53 which is filled with a cobalt-based catalyst for instance, thereby allowing the hydrogen and carbon monoxide all included in the synthesis gas to react with each other, thus synthesizing gasoline, kerosene and gas oil at a high yield.

By the way, in the foregoing embodiment, the carbon dioxide to be added to the natural gas is procured by recovering carbon dioxide from the combustion exhaust gas generated at the combustion radiation portion or from the synthesis gas. However, the carbon dioxide can be procured from different sources. For example, it is possible to employ carbon dioxide that can be recovered from the combustion exhaust gas generated at the boiler, or carbon dioxide which has been discarded in other plants. Namely, the carbon dioxide that has been discarded in other plants can be effectively utilized as a raw material in the method of manufacturing methanol according to this invention, so that it is now possible to reduce the quantity of carbon dioxide to be released into air atmosphere, thereby contributing to the prevention of the warm-up of the globe.

In the foregoing embodiment, the synthesis gas manufactured in the reformer is introduced into the Fisher-Tropsch reaction system so as to synthesize gasoline, etc. However, the synthesis gas manufactured in the reformer can be also applied to the synthesis of methanol or dimethyl ether.

As explained above, it is possible according to this invention to effectively utilize the carbon dioxide in a natural gas containing hydrogen sulfide and carbon dioxide by selectively removing only

the hydrogen sulfide therefrom in a method for manufacturing a synthesis gas from the natural gas containing hydrogen sulfide and carbon dioxide by making use of a reformer, thereby making it possible to
5 reduce the quantity of carbon dioxide to be added to the natural gas prior to the stage where the natural gas is to be transferred to the reformer. Further, it is also possible according to this invention to provide a method of manufacturing a synthesis gas which is
10 suited for the synthesis of gasoline, kerosene and gas oil by way of the Fisher-Tropsch reaction system, or for the synthesis of methanol or dimethyl ether at low cost.

Additional advantages and modifications will
15 readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the
20 spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.